

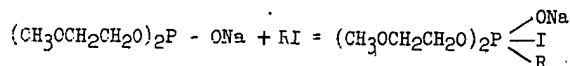
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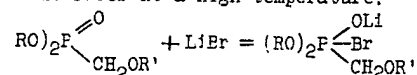
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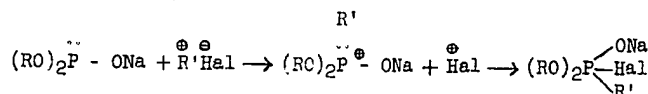
The mechanism of this reaction is considered to be either an exchange of metal for the hydrocarbon radical, if the structure of the salt is assumed to be based on pentavalent phosphorus, or as an addition of the alkyl halide to the phosphorus accompanied by the subsequent detachment of the metal halide, if the structure of the salt is assumed to be based on trivalent phosphorus. The most probable mechanism of this reaction, in our opinion, is the addition of the alkyl halide to the salts of phosphorous acid. This is confirmed, as we have shown, by the formation of products of the addition of iodides to sodium di-beta-methoxyethylphosphite in the course of the usual reaction of Michaelis-Becker,



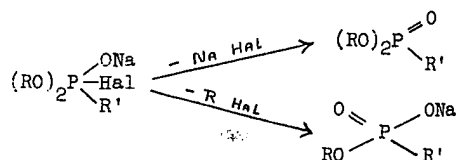
and the formation of products of addition of halogen salts of lithium (LiBr, LiI) with esters of alkoxyethylphosphonic acid as a result of the action of the lithium halide on the ester at a high temperature:



A further development of the ideas introduced into the field of organic phosphorus compounds by Academician A. Ye. Arbuzov and successfully applied by the Kazan' school of chemists under his leadership, in the explanation of the reaction of halogen compounds with salts of dialkylphosphorous acids, is the addition of the positively charged atom of carbon from the alkyl halide to the phosphorus, the latter carrying an isolated pair of electrons. This reaction scheme is shown below.

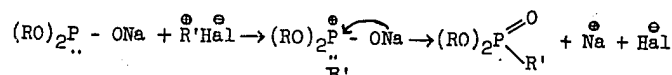


Splitting off of either sodium halide or alkyl halide follows:



The direction in which the splitting proceeds depends principally on the nature of the radical joined to the phosphorus, but also on the nature of the halide and ester radicals (intramolecular causes) and on the conditions under which the experiments are conducted.

The formation of esters of alkylphosphonic acids can be explained also by another course of the reaction:



The sodium ion and halide ion give sodium halide.

From such an explanation of the principle of the reaction, it follows that not only halogen compounds, but also other substances whose molecules are polarized similarly to those of the halogen compounds, can react with the salts of

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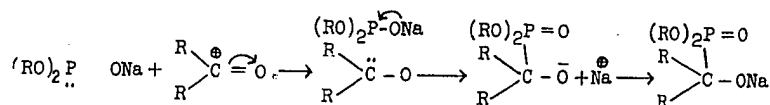
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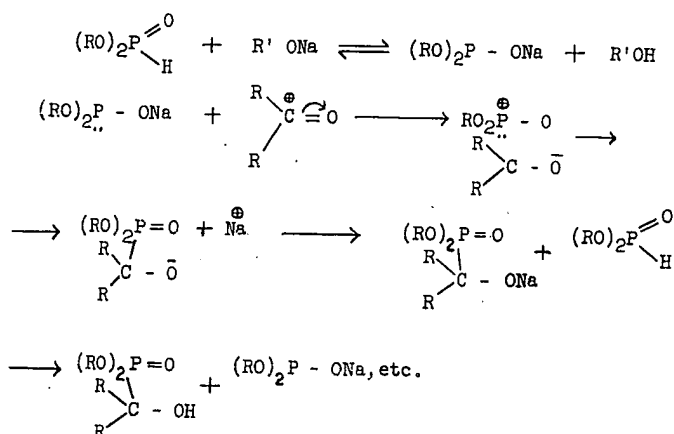
dialkylphosphorous acids. Naturally, this analogy can be extended also to cover aldehydes and ketones whose molecules are polarized. The oxygen of the carbonyl group draws electrons from the carbon-oxygen bond and makes the carbon of the carbonyl groups positively charged, i.e., capable of interaction with the isolated pair of electrons of the phosphorus in the salts of dialkylphosphorous acids:



Upon treatment of the compound thus formed with acidified water, the ester of alpha-hydroxyalkylphosphonic acid is obtained.

The addition of sodium diethylphosphite to the carbonyl group of alpha-ketophosphonic acids was first suggested by A. Ye. Arbuzov and M. M. Azanovskaya (9) in explaining the reaction of acetyl chloride on sodium diethylphosphite.

Arbuzov and A. N. Pudovik (10) showed that dialkylphosphorous acids are added to an ethylene bond which is activated by a nitrile, carbonyl, or carboxyl group in the presence of sodium alcoholate. The method indicated by us was applied to the reactions of aldehydes and ketones on dialkylphosphorous acids. Alcoholates of alkaline metals, enolating the dialkylphosphorous acid, enable this reaction to take place. In practice in experiments several drops of lithium or sodium methylate are usually employed. The reaction is expressed by the scheme:



The chain reaction progresses rapidly, generating a great amount of heat and giving a very good yield. The degree of completeness of the reaction depends on the radicals of the carbonyl group: if the radicals strengthen the effect of polarization of the molecules, then the reaction proceeds vigorously, resulting almost in a quantitative yield (for example, in the case of benzaldehyde); if, on the other hand, the radicals reduce the effect of polarization of the molecules, then the reaction proceeds at a moderate speed and the yield is correspondingly lowered. We obtained methyl, ethyl, and isopropyl esters of alpha-hydroxymethyl-, ethyl, isopropyl-, butyl-, benzyl-, cyclopentyl-, cyclohexyl-, and other phosphonic acids -- in all, more than 30 new substances. The products obtained were crystalline substances with well developed crystalline forms or thick viscous liquids.

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Esters of alpha-hydroxyalkylphosphonic acids can be subjected to further transformations: elimination of water produces unsaturated alkylphosphonic acids, and the substitution of a hydrocarbon radical for an atom of hydrogen in the hydroxyl group produces esters of alpha-alkoxyalkylphosphonic acids.

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